

REACTION KINETICS IN SUPERCRITICAL FLUIDS

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KEYWORDS: supercritical fluids, kinetics, AIBN, jet fuel oxidation

INTRODUCTION

Supercritical fluids constitute a unique medium for synthesis and processing, particularly near the critical point of the solvent where large changes in solvent properties can be obtained with relatively small changes in pressure. There is relatively little information available concerning the impact of pressure on reaction rates in the vicinity of the solvent critical point, particularly in free-radical processes. In studies of spin-exchange reactions between nitroxide free radicals near the critical point of ethane, Randolph and Carlier (1) found that rate constants were independent of radical concentrations. However, extreme effects of local radical density augmentation were observed due to solvent clustering near the critical point. Cluster lifetimes compared to solute-solute collision probabilities were a determining factor in the ten-fold increase in reaction rates at the critical point. The nature of the transition state will determine how solvent clustering and reactant mobilities will impact reaction rates as the solvent moves from sub- to supercritical conditions. First-order rate constants for the thermal decomposition of α -chlorobenzyl methyl ether in supercritical 1,1-difluoroethane demonstrated (2) that the greatest impact of small changes in pressure on the rate constants were in those regions where the solvent compressibility was high, i.e., near the critical point. This was explained in terms of changes in dielectric strength of the supercritical solvent, which can influence the solvatochromic transition energy. Partial molar volumes of solutes can reach negative thousands of cm³/mol in highly compressible near-critical fluids in contrast to very small values in liquid solvents. Such large negative activation volumes and entropies suggest that solvent clusters are more ordered around the transition state than the reactants. Such solvent clustering will exert a significant impact on the reactivity of free radicals in a supercritical fluid.

As fuel temperatures approach approximately 350° - 375°C, many researchers have observed a decline in the amounts of thermal deposits. This has been explained in terms of chemical and physical effects. Since hydroperoxides thermally decompose at approximately 280 - 300°C, this was taken as evidence that deposition is linked to the presence of hydroperoxides. Another explanation proposed for this behavior is that, at these temperatures, components of the fuel can reach a supercritical state. Thus, the increased solvency of the supercritical fuel components was thought to be responsible for redissolving the insoluble products. The critical point of JP-5 fuel has been calculated(3) to occur in the range of 382° - 415°C at 300 - 380 psi (21 - 26 bar). In a series of single tube heat exchanger experiments, Edwards and Zabarnick (4) demonstrated that fuel oxidation chemistry was the determining factor in the amounts of insoluble products formed under those conditions and not simple supercritical solvency effects. However, this work did not address the impact of supercritical conditions on the free radical chemistry. Fuels subjected to conditions where components can reach their critical point may undergo chemical changes that would not necessarily form insoluble products at that time. Electron transfer reactions between metals and fuel constituents would also be mediated by solvent cluster lifetimes, which may play a role in the influence of catalytic metals on fuel properties.

In an effort to bridge the gap between gas phase and liquid phase chemistry, this work has been directed towards elucidating the impact of temperature and pressure on the free radical autoxidation mechanism of hydrocarbons near the critical point. This paper describes the apparatus and methods developed to obtain *in-situ* measurements of reaction kinetics in sub- and supercritical solvents. Some preliminary results of kinetic

measurements of the thermal decomposition of a free-radical initiator, 2,2'-azobis(isobutyronitrile) (AIBN) in supercritical CO₂ are presented.

EXPERIMENTAL

Materials. Carbon dioxide (SCF grade 99.99%, Matheson) was passed through a Chromtech high pressure oxygen and moisture trap and a Chromtech high pressure activated carbon trap to remove hydrocarbons. 2,2'-azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was recrystallized from methanol.

Apparatus. The apparatus used to perform *in-situ* optical kinetic measurements is shown in Figure 1. Two ISCO type 100DX 100 mL syringe pumps were coupled via a check valve assembly to allow operation in dual pump mode, to facilitate rapid filling and pressure equilibration of the reactor. The pump cylinders were cooled to facilitate rapid filling. A Rheodyne injection valve was incorporated in a sampling loop to allow for the introduction of liquid modifiers or reactants into the gas stream. A Parr high pressure stirred mini-reactor was fitted with two 2.5 cm dia. x 1.3 cm thick fused silica windows located near the bottom, 180° apart. Reactor vessels with internal volumes of 25 and 450 mL were used in the kinetic experiments. The reactor was fitted with a pressure transducer and a variable restrictor to provide a means for sampling during an experiment for analysis.

Kinetic measurements were obtained optically over the range of 180 to 650 nm. A xenon arc lamp was coupled to a fused silica fiber optic bundle which was focused through the reactor window onto another fiber optic bundle interfaced to an Oriel Multispec 1/8 meter spectrograph. A grating was used that provided a bandpass of 164 nm at a resolution of 0.4 nm with a 50 μ slit. An Oriel Instaspec II 1024 channel photodiode array (PDA) was operated with a personal computer, which allowed for data acquisition at a maximum rate of 62 kHz. Software routines were written to acquire background corrected PDA counts and absorbance measurements at predefined intervals.

Characterization of AIBN decomposition at sub-critical conditions was performed with a HP 6890 gas chromatograph equipped with a nitrogen specific detector. Product characterization was performed using an HP 5890 gas chromatograph with a Finnigan ion trap mass spectrometer detector.

Kinetic Procedure. The reactant was placed in the reactor and purged with argon for 5 - 10 minutes then with SFC grade CO₂ for one minute. The reactor was then pressurized to approximately 75.8 bar (1100 psi). After the reactor reached thermal equilibrium, the pressure was adjusted to the desired final pressure by addition of CO₂. Optical measurements, in background corrected PDA counts, were obtained every 15 min for up to 8 hours. First-order rates were determined from photometric absorbance calculated from the acquired optical measurements.

RESULTS AND DISCUSSION

In order to study the impact of supercritical solvents on the mechanism of hydrocarbon autoxidation, a model compound that constitutes a convenient source of free-radicals was first examined. The compound, 2,2'-azobis(isobutyronitrile) (AIBN) is commonly used as a free-radical polymerization initiator. The thermal decomposition of AIBN is well known and has been studied in supercritical CO₂ by DeSimone, et al (5). In the initial phase of this study, the kinetics of the thermal decomposition of AIBN were examined in the kinetic reactor described above in supercritical CO₂ at a pressure of 172 bar (2500 psi) and compared with their earlier work (5) performed at 276 bar (4000 psi).

As shown in Figure 2, thermolysis of AIBN generates free-radicals which have been proposed (6) to form in solvent cages. These radicals can either diffuse out of these cages or dimerize to form a transient keteimine adduct (II) that can, in turn dissociate

to regenerate the radicals. Solvent-solute interactions would exert an effect on the relative rates of diffusion out of the solvent cage and combination within the cage to form the adduct shown. Lower AIBN decomposition rates reported (5) in carbon dioxide compared with benzene illustrate the polar nature of the transition state and the impact of local changes in solvent dielectric properties. GC-MS analysis of AIBN in thermally stressed sub-critical benzene in the gas phase shows evidence of concurrent formation of compound II with a decrease in the abundance of the free radicals.

From absorbance measurements obtained during a typical kinetic experiment in supercritical CO₂ at 60°C and 172 bar, AIBN absorbance is shown (Figure 4) at 354.8nm and compound II at 290.1. The corresponding first-order plots of AIBN decomposition and the intermediate formation are shown in Figure 5. From the slopes of these plots, the rate constants (k_1) were calculated at 172 bar to be $7.4 \times 10^{-5} \text{ s}^{-1}$, $1.5 \times 10^{-5} \text{ s}^{-1}$ and $4.8 \times 10^{-5} \text{ s}^{-1}$ at 40, 50 and 60°C, respectively. The Arrhenius treatment of these data indicated the activation energy for thermal decomposition of AIBN in these experiments to be 80.9 kJ·mol⁻¹.

The activation volume of species (x) is often expressed as $\Delta v^\ddagger = -RT (\ln k_x / dp)_T$. To examine the effect of pressure on the formation rate of II, kinetic measurements were obtained as a function of pressure at 50°C from 76 to 172 bar. The effect of pressure is clearly shown in Figure 6, where the first-order formation constants (k_2) are plotted against pressure. While dielectric changes in carbon dioxide would be small at high pressures, in this region near the critical pressure of CO₂ (73.8 bar), the compressibility is high and local changes in dielectric properties can change by large amounts with small pressure changes. From a plot of the logarithm of k_2 vs pressure, the activation volume for the intermediate product was estimated to be -143 cc/mole.

SUMMARY

Real-time measurements of reaction kinetics in supercritical solvents has been demonstrated by examination of a model free radical source. However, while the kinetic rates measured in these experiments were self-consistent, they are higher by from 3 to 9 times than the values reported (5) for k_1 at 276 bar. Moreover, the activation energy determined from these measurements was also lower than expected. Current efforts are underway to resolve these discrepancies before the work is extended to include radical trapping compounds and hydroperoxides.

ACKNOWLEDGEMENTS

Funding for this work was provided by the Office of Naval Research.

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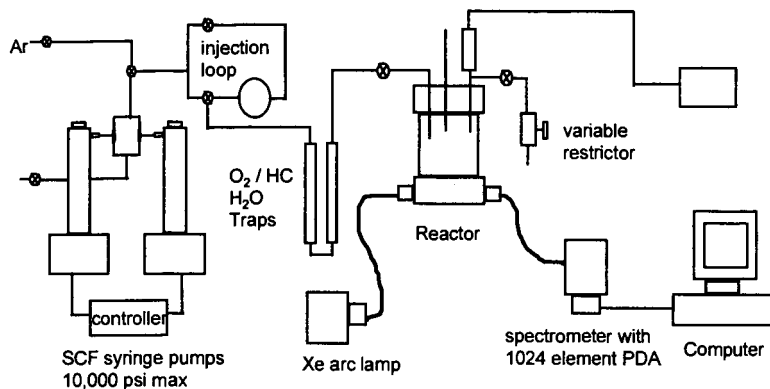


Figure 1. Schematic representation of apparatus for performing kinetic measurements in supercritical media.

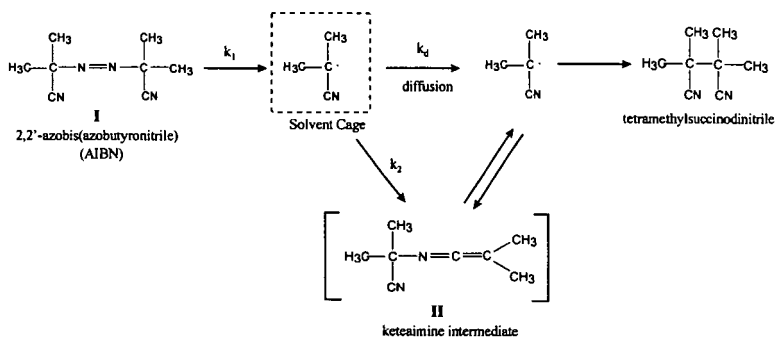


Figure 2. Thermal decomposition mechanism of AIBN (DeSimone, 1993)

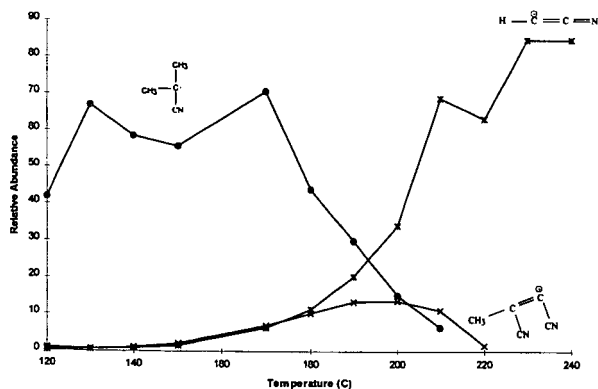


Figure 3. Major thermal decomposition products of AIBN in benzene at sub-critical conditions.

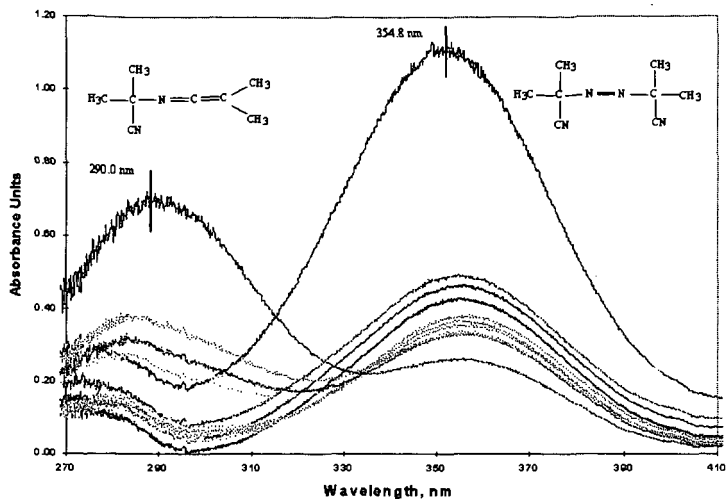


Figure 4. Absorption characteristics of AIBN thermal decomposition of AIBN in supercritical CO_2 at 60°C and 172 bar (not all scans shown).

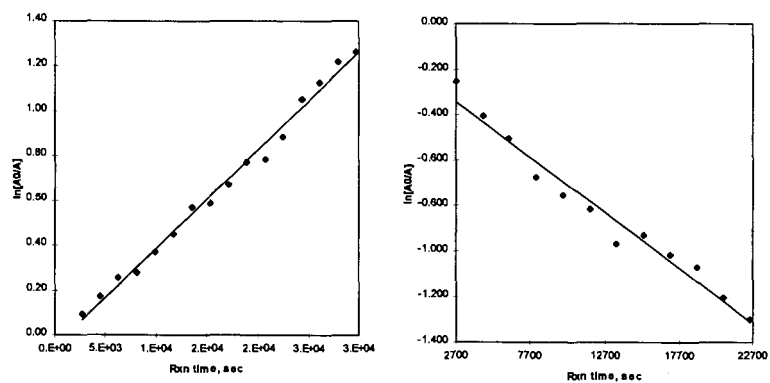


Figure 5. First order plots of AIBN thermal decomposition (left chart) and intermediate formation (right chart).

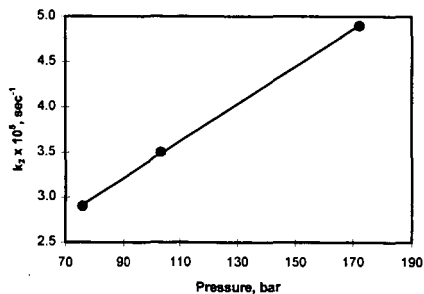


Figure 6. Variation of first order formation rate of ketamine intermediate with pressure.